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(71) Anmelder:
BASF AG, 67063 Ludwigshafen, DE

(72) Erfinder:
Bartsch, Michael, Dr., 67433 Neustadt, DE;
Baumann, Robert, Dr., 68161 Mannheim, DE;
Haderlein, Gerd, Dr., 67269 Grünstadt, DE; Flores,
Miguel, Dr., Aranjuez, ES; Jungkamp, Tim, Dr.,
69207 Sandhausen, DE; Luyken, Hermann, 67069
Ludwigshafen, DE; Scheidel, Jens, Dr., 69493
Hirschberg, DE; Siegel, Wolfgang, Dr., 67117
Limburgerhof, DE; Kunsmann-Keitel, Dagmar
Pascale, Dr., 67117 Limburgerhof, DE

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: **Verfahren zur Isomerisierung von 2-Methyl-3-butennitril zu linearem Pentennitril**

(57) Zusammenfassung: Verfahren zur Isomerisierung von 2-Methyl-3-butennitril zu linearem Pentennitril in Gegenwart eines Systems, enthaltend

a) Ni(O)

b) eine Ni(O) als Ligand komplexierende, dreibindigen Phosphor enthaltende Verbindung und

c) eine Lewis-Säure,

dadurch gekennzeichnet, dass man während der Isomerisierung dem Reaktionsgemisch eine Mischung, enthaltend 2-Methyl-3-butennitril und lineares Pentennitril, entnimmt.

English Translation of

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(2a)

Isomerization of 2-methyl-3-butenitrile to linear pentenenitrile

The present invention relates to a process for isomerizing 2-methyl-3-butenitrile to linear pentenenitrile in the presence of a system comprising

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- a) Ni(0)
- b) a trivalent phosphorus-containing compound which complexes Ni(0) as a ligand and
- c) a Lewis acid,

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which comprises withdrawing a mixture comprising 2-methyl-3-butenitrile and linear pentenenitrile from the reaction mixture during the isomerization.

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2-Methyl-3-butenitrile is formed in significant amounts as a by-product in the hydrocyanation, in the presence of a catalyst, of butadiene to linear pentenenitrile, such as 3-pentenenitrile. Depending on the catalyst used, the molar ratio of 2-methyl-3-butenitrile to 3-pentenenitrile may be up to 2:1.

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3-Pentenenitrile is converted industrially on a large scale to adiponitrile which itself constitutes an important starting compound for preparing polyamides, in particular the industrially significant polyamides polyamide-6 (nylon-6) and polyamide-6,6 (nylon-6,6).

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In order to be able to likewise utilize 2-methyl-3-butenitrile for the preparation of adiponitrile, processes have been proposed for isomerizing 2-methyl-3-butenitrile to linear pentenenitrile, in particular 3-pentenenitrile.

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For instance, US 3,676,481 in column 52, lines 48-50 and the examples, describes the batchwise isomerization of 2-methyl-3-butenitrile in the presence of Ni(0), a phosphite ligand and certain Lewis acids at elevated temperatures. After the isomerization, the resulting product mixture is distilled off from the catalyst system, likewise at elevated temperatures.

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A disadvantage of this process is the high delay times during the isomerization, the high thermal stress on the thermally sensitive catalyst during the isomerization and also the high thermal stress on the thermally sensitive catalyst during the subsequent

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distillation. The high thermal stress on the catalyst leads to undesired degradation of the catalyst.

5 It is an object of the present invention to provide a process which enables the isomerization of 2-methyl-3-butenitrile to linear pentenenitrile, in particular 3-pentenenitrile, in a technically simple and economical manner.

We have found that this object is achieved by the process defined at the outset.

10 According to the invention, 2-methyl-3-butenitrile is isomerized.

Numerous processes for preparing 2-methyl-3-butenitrile or mixtures which comprise 2-methyl-3-butenitrile, especially in addition to linear pentenenitriles, are known.

15 In addition to 2-methyl-3-butenitrile as a pure compound, those mixtures which comprise 2-methyl-3-butenitrile, in particular in addition to linear pentenenitrile, can be used in the process according to the invention. In the context of the present invention, the term 2-methyl-3-butenitrile includes both the pure compound mentioned and such mixtures.

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It has been found to be advantageous to deplete the compounds present in addition to 2-methyl-3-butenitrile from such mixtures, for example by distillation. Especially in the case of depletion of linear pentenenitrile from such mixtures, it is advantageous to increase the space-time yield in the process according to the invention.

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According to the invention, the isomerization is carried out in the presence of a system comprising

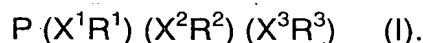
- a) Ni(0)
- 30 b) a trivalent phosphorus-containing compound which complexes Ni(0) as a ligand and
- c) a Lewis acid.

The preparation of Ni(0)-containing catalyst systems is known per se and, for the
35 purposes of the present invention, can be effected by processes known per se.

Moreover, the system additionally comprises a compound which is suitable as a ligand for Ni(0) and contains at least one trivalent phosphorus atom, or a mixture of such compounds.

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In a preferred embodiment, the compound suitable as a ligand may be one of the formula



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In the context of the present invention, this compound is a single compound or a mixture of different compounds of the aforementioned formula.

X^1 , X^2 , X^3 may each independently be oxygen or a single bond.

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When all of the X^1 , X^2 and X^3 groups are single bonds, compound (I) is a phosphine of the formula $P(R^1 R^2 R^3)$ with the definitions of R^1 , R^2 and R^3 specified in this description.

20 When two of the X^1 , X^2 and X^3 groups are single bonds and one is oxygen, compound (I) is a phosphinite of the formula $P(OR^1)(R^2)(R^3)$ or $P(R^1)(OR^2)(R^3)$ or $P(R^1)(R^2)(OR^3)$ with the definitions of R^1 , R^2 and R^3 specified in this description.

25 When one of the X^1 , X^2 and X^3 groups is a single bond and two are oxygen, compound (I) is a phosphonite of the formula $P(OR^1)(OR^2)(R^3)$ or $P(R^1)(OR^2)(OR^3)$ or $P(OR^1)(R^2)(OR^3)$ with the definitions of R^1 , R^2 and R^3 specified in this description.

30 In a preferred embodiment, all X^1 , X^2 and X^3 groups should be oxygen, so that compound (I) is advantageously a phosphite of the formula $P(OR^1)(OR^2)(OR^3)$ with the definitions of R^1 , R^2 and R^3 specified in this description.

According to the invention, R^1 , R^2 , R^3 are each independently identical or different organic radicals.

35 R^1 , R^2 and R^3 are each independently alkyl radicals, advantageously having from 1 to 10 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, aryl groups such as phenyl, o-tolyl, m-tolyl, p-tolyl, 1-naphthyl, 2-naphthyl, or

hydrocarbyl, advantageously having from 1 to 20 carbon atoms, such as 1,1'-biphenol, 1,1'-binaphthol.

5 The R^1 , R^2 and R^3 groups may be bonded together directly, i.e. not solely via the central phosphorus atom. Preference is given to the R^1 , R^2 and R^3 groups not being bonded together directly.

10 In a preferred embodiment, R^1 , R^2 and R^3 are radicals selected from the group consisting of phenyl, o-tolyl, m-tolyl and p-tolyl.

In a particularly preferred embodiment, a maximum of two of the R^1 , R^2 and R^3 groups should be phenyl groups.

15 In another preferred embodiment, a maximum of two of the R^1 , R^2 and R^3 groups should be o-tolyl groups.

Particularly preferred compounds which may be used are those of the formula $(o\text{-tolyl-O})_w (m\text{-tolyl-O})_x (p\text{-tolyl-O})_y (\text{phenyl-O})_z P$

where w, x, y, z are each a natural number

20 where $w + x + y + z = 3$ and

w, z are each less than or equal to 2,

such as $(p\text{-tolyl-O})(\text{phenyl})_2P$, $(m\text{-tolyl-O})(\text{phenyl})_2P$, $(o\text{-tolyl-O})(\text{phenyl})_2P$, $(p\text{-tolyl-O})_2(\text{phenyl})P$, $(m\text{-tolyl-O})_2(\text{phenyl})P$, $(o\text{-tolyl-O})_2(\text{phenyl})P$, $(m\text{-tolyl-O})(p\text{-tolyl-O})(\text{phenyl})P$, $(o\text{-tolyl-O})(p\text{-tolyl-O})(\text{phenyl})P$, $(o\text{-tolyl-O})(m\text{-tolyl-O})(\text{phenyl})P$, $(p\text{-tolyl-O})_3P$, $(m\text{-tolyl-O})(p\text{-tolyl-O})_2P$, $(o\text{-tolyl-O})(p\text{-tolyl-O})_2P$, $(m\text{-tolyl-O})_2(p\text{-tolyl-O})P$, $(o\text{-tolyl-O})_2(p\text{-tolyl-O})P$, $(o\text{-tolyl-O})(m\text{-tolyl-O})(p\text{-tolyl-O})P$, $(m\text{-tolyl-O})_3P$, $(o\text{-tolyl-O})(m\text{-tolyl-O})_2P$, $(o\text{-tolyl-O})_2(m\text{-tolyl-O})P$ or mixtures of such compounds.

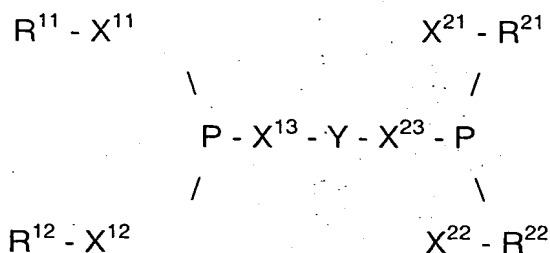
30 For example, mixtures comprising $(m\text{-tolyl-O})_3P$, $(m\text{-tolyl-O})_2(p\text{-tolyl-O})P$, $(m\text{-tolyl-O})(p\text{-tolyl-O})_2P$ and $(p\text{-tolyl-O})_3P$ may be obtained by reacting a mixture comprising m-cresol and p-cresol, in particular in a molar ratio of 2:1, as obtained in the distillative workup of crude oil, with a phosphorus trihalide, such as phosphorus trichloride.

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Such compounds and their preparation are known per se.

In a further preferred embodiment, the compound suitable as a ligand for Ni(0) may be one of the formula

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where

- $X^{11}, X^{12}, X^{13}, X^{21}, X^{22}, X^{23}$ are each independently oxygen or a single bond
 R^{11}, R^{12} are each independently identical or different, individual or bridged organic radicals
 R^{21}, R^{22} are each independently identical or different, individual or bridged organic radicals,
 Y is a bridging group.

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- 15 In the context of the present invention, such a compound is a single compound or a mixture of different compounds of the aforementioned formula.

In a preferred embodiment, $X^{11}, X^{12}, X^{13}, X^{21}, X^{22}, X^{23}$ may each be oxygen. In such a case, the bridging group Y is bonded to phosphite groups.

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- In another preferred embodiment, X^{11} and X^{12} may each be oxygen and X^{13} a single bond, or X^{11} and X^{13} oxygen and X^{12} a single bond, so that the phosphorus atom surrounded by X^{11}, X^{12} and X^{13} is the central atom of a phosphonite. In such a case, X^{21}, X^{22} and X^{23} may be oxygen, or X^{21} and X^{22} may each be oxygen and X^{23} a single bond, or X^{21} and X^{23} may each be oxygen and X^{22} a single bond, or X^{23} may be oxygen and X^{21} and X^{22} each a single bond, or X^{21} may be oxygen and X^{22} and X^{23} each a single bond, or X^{21}, X^{22} and X^{23} may each be a single bond, so that the phosphorus atom surrounded by X^{21}, X^{22} and X^{23} may be a phosphite, phosphonite, phosphinite or phosphine, preferably a phosphonite.

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- In another preferred embodiment, X^{13} may be oxygen and X^{11} and X^{12} each a single bond, or X^{11} may be oxygen and X^{12} and X^{13} each a single bond, so that the phosphorus atom surrounded by X^{11}, X^{12} and X^{13} is the central atom of a phosphinite. In such a case, X^{21}, X^{22} and X^{23} may each be oxygen, or X^{23} may be oxygen and X^{21} and X^{22} a single bond, or X^{21} may be oxygen and X^{22} and X^{23} each a single bond, or X^{21}, X^{22} and X^{23} may each be a single bond, so that the phosphorus atom surrounded by X^{21}, X^{22} and X^{23} may be the central atom of a phosphite, phosphinite or phosphine, preferably a phosphinite.

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In another preferred embodiment, X^{11} , X^{12} and X^{13} may each be a single bond, so that the phosphorus atom surrounded by X^{11} , X^{12} and X^{13} is the central atom of a phosphine. In such a case, X^{21} , X^{22} and X^{23} may each be oxygen, or X^{21} , X^{22} and X^{23} may each be a single bond, so that the phosphorus atom surrounded by X^{21} , X^{22} and X^{23} may be the central atom of a phosphite or phosphine, preferably a phosphine.

The bridging group Y is advantageously an aryl group which is substituted, for example by C₁-C₄-alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or is unsubstituted, preferably a group having from 6 to 20 carbon atoms in the aromatic system, in particular pyrocatechol, bis(phenol) or bis(naphthol).

The R^{11} and R^{12} radicals may each independently be the same or different organic radicals. Advantageous R^{11} and R^{12} radicals are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by C₁-C₄-alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups.

The R^{21} and R^{22} radicals may each independently be the same or different organic radicals. Advantageous R^{21} and R^{22} radicals are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by C₁-C₄-alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups.

The R^{11} and R^{12} radicals may each be separate or bridged.

The R^{21} and R^{22} radicals may each be separate or bridged.

The R^{11} , R^{12} , R^{21} and R^{22} radicals may each be separate, two may be bridged and two separate, or all four may be bridged, in the manner described.

In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV and V specified in US 5,723,641.

In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI and VII specified in US 5,512,696, in particular the compounds used there in examples 1 to 31.

In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV and XV specified in US 5,821,378, in particular the compounds used there in examples 1 to 73.

- 5 In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V and VI specified in US 5,512,695, in particular the compounds used there in examples 1 to 6.

- 10 In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII and XIV specified in US 5,981,772, in particular the compounds used there in examples 1 to 66.

- 15 In a particularly preferred embodiment, useful compounds are those specified in US 6,127,567 and the compounds used there in examples 1 to 29.

- In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX and X specified in US 6,020,516, in particular the compounds used there in examples 1 to 33.

- 20 In a particularly preferred embodiment, useful compounds are those specified in US 5,959,135, and the compounds used there in examples 1 to 13.

- 25 In a particularly preferred embodiment, useful compounds are those of the formula I, II and III specified in US 5,847,191.

- In a particularly preferred embodiment, useful compounds are those specified in US 5,523,453, in particular the compounds illustrated there in formula 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 and 21.

- 30 In a particularly preferred embodiment, useful compounds are those specified in WO 01/14392, preferably the compounds illustrated there in formula V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII, XXI, XXII, XXIII.

- 35 In a particularly preferred embodiment, useful compounds are those specified in WO 98/27054.

In a particularly preferred embodiment, useful compounds are those specified in WO 99/13983.

In a particularly preferred embodiment, useful compounds are those specified in WO 99/64155.

5. In a particularly preferred embodiment, useful compounds are those specified in the German laid-open specification DE 10038037.

In a particularly preferred embodiment, useful compounds are those specified in German laid-open specification DE 10046025.

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Such compounds and their preparation are known per se.

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In a further preferred embodiment, a mixture of one or more of the aforementioned compounds which are suitable as a ligand for Ni(0) and contain one phosphorus atom, and one or more compounds which are suitable as a ligand for Ni(0) and contain two phosphorus atoms can be employed.

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In a particularly preferred embodiment, useful systems are those which are specified in the international patent application PCT/EP02/07888 and comprise Ni(0) and such mixtures.

In addition, the system comprises a Lewis acid.

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In the context of the present invention, a Lewis acid is either a single Lewis acid or else a mixture of a plurality of, for example two, three or four, Lewis acids.

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Useful Lewis acids are inorganic or organic metal compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr_2 , ZnI_2 , ZnCl_2 , ZnSO_4 , CuCl_2 , CuCl , $\text{Cu}(\text{O}_3\text{SCF}_3)_2$, CoCl_2 , CoI_2 , FeI_2 , FeCl_3 , FeCl_2 , $\text{FeCl}_2(\text{THF})_2$, $\text{TiCl}_4(\text{THF})_2$, TiCl_4 , TiCl_3 , $\text{CITi}(\text{O}-i\text{-propyl})_3$, MnCl_2 , ScCl_3 , AlCl_3 , $(\text{C}_8\text{H}_{17})\text{AlCl}_2$, $(\text{C}_8\text{H}_{17})_2\text{AlCl}$, $(i\text{-C}_4\text{H}_9)_2\text{AlCl}$, $(\text{C}_6\text{H}_5)_2\text{AlCl}$, $(\text{C}_6\text{H}_5)\text{AlCl}_2$, ReCl_5 , ZrCl_4 , NbCl_5 , VCl_3 , CrCl_2 , MoCl_5 , YCl_3 , CdCl_2 , LaCl_3 , $\text{Er}(\text{O}_3\text{SCF}_3)_3$, $\text{Yb}(\text{O}_2\text{CCF}_3)_3$, SmCl_3 , $\text{B}(\text{C}_6\text{H}_5)_3$, TaCl_5 , as described, for example, in US 6,127,567, US 6,171,996 and US 6,380,421. Also useful are metal salts such as ZnCl_2 , CoI_2 and SnCl_2 , and organometallic compounds such as RAlCl_2 , R_2AlCl , $\text{R}_3\text{SnO}_3\text{SCF}_3$ and R_3B , where R is an alkyl or aryl group, as described, for example, in US 3,496,217, US 3,496,218 and US 4,774,353. According to

US 3,773,809, the promoter used may be a metal in cationic form which is selected from a group consisting of zinc, cadmium, beryllium, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, erbium, germanium, tin, vanadium, niobium, scandium, chromium, molybdenum, tungsten, manganese, rhenium, palladium, thorium, iron and cobalt, preferably zinc, cadmium, titanium, tin, chromium, iron and cobalt, and the anionic moiety of the compound may be selected from the group consisting of halides such as fluoride, chloride, bromide and iodide, anions of lower fatty acids having from 2 to 7 carbon atoms, HPO_3^{2-} , H_3PO^{2-} , CF_3COO^- , $\text{C}_7\text{H}_{15}\text{OSO}_2^-$ or SO_4^{2-} . Further suitable promoters disclosed by US 3,773,809 are borohydrides, organoborohydrides and boric esters of the formula R_3B and B(OR)_3 , where R is selected from the group consisting of hydrogen, aryl radicals having from 6 to 18 carbon atoms, aryl radicals substituted by alkyl groups having from 1 to 7 carbon atoms and aryl radicals substituted by cyano-substituted alkyl groups having from 1 to 7 carbon atoms, advantageously triphenylboron. Moreover, as described in US 4,874,884, it is possible to use synergistically active combinations of Lewis acids, in order to increase the activity of the catalyst system. Suitable promoters may, for example, be selected from the group consisting of CdCl_2 , FeCl_2 , ZnCl_2 , $\text{B(C}_6\text{H}_5)_3$ and $(\text{C}_6\text{H}_5)_3\text{SnX}$, where $\text{X}=\text{CF}_3\text{SO}_3$, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$ or $(\text{C}_6\text{H}_5)_3\text{BCN}$, and the preferred ratio specified of promoter to nickel is from about 1:16 to about 50:1.

In the context of the present invention, the term Lewis acid also includes the promoters specified in US 3,496,217, US 3,496,218, US 4,774,353, US 4,874,884, US 6,127,567, US 6,171,996 and US 6,380,421.

Particularly preferred Lewis acids among those mentioned are in particular metal salts, more preferably metal halides, such as fluorides, chlorides, bromides, iodides, in particular chlorides, of which particular preference is given to zinc chloride, iron(II) chloride and iron(III) chloride.

According to the invention, the isomerization results in linear pentenenitrile.

In the context of the present invention, the term linear pentenenitrile refers to a single such isomer or a mixture of 2, 3, 4 or 5 different such isomers.

The linear pentenenitrile may be cis-2-pentenenitrile, trans-2-pentenenitrile, cis-3-pentenenitrile, trans-3-pentenenitrile, 4-pentenenitrile or mixtures thereof, preferably cis-3-pentenenitrile, trans-3-pentenenitrile, 4-pentenenitrile or mixtures thereof, in particular cis-3-pentenenitrile, trans-3-pentenenitrile or mixtures thereof, which, in the

context of the present invention, are referred to as 3-pentenitrile, both in each case individually and as a mixture.

5 The isomerization can be carried out in the presence of a liquid diluent, for example a hydrocarbon such as hexane, heptane, octane, cyclohexane, methylcyclohexane, benzene, for example an ether such as diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole, for example an ester such as ethyl acetate, methyl benzoate, or for example a nitrile such as acetonitrile, benzonitrile, or mixtures of such diluents. In a preferred embodiment, isomerization is effected in the absence of such a liquid
10 diluent.

It has further been found to be advantageous to carry out the isomerization in a nonoxidizing atmosphere, such as under a protective gas atmosphere of nitrogen or a noble gas such as argon.
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According to the invention, during the isomerization, a mixture comprising 2-methyl-3-butenitrile and linear pentenenitrile is withdrawn from the reaction mixture.

20 In a preferred embodiment, a stream comprising 2-methyl-3-butenitrile and linear pentenenitrile, preferably consisting of 2-methyl-3-butenitrile and linear pentenenitrile, is withdrawn continuously or quasi-continuously, preferably continuously. In addition, a stream comprising 2-methyl-3-butenitrile is fed continuously or quasi-continuously, preferably continuously.

25 In a preferred embodiment, the feed stream may have a content of 2-methyl-3-butenitrile in the range from 10 to 100% by weight, preferably from 80 to 100% by weight.

30 In a preferred embodiment, the withdrawal stream may have a content of 2-methyl-3-butenitrile in the range from 5 to 80% by weight, preferably from 20 to 60% by weight, and a content of linear pentenenitrile in the range from 20 to 95% by weight, preferably from 40 to 80% by weight, with the proviso that the sum of the contents of 2-methyl-3-butenitrile and linear pentenenitrile is at most 100% by weight.

35 The withdrawal may advantageously be distillative.

Useful apparatus for the distillation is apparatus customary for this purpose, as described, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd

Ed., Vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or columns having random packing.

- 5 It is equally possible to withdraw directly from the reactor without separating stages.

The composition of the withdrawal stream with regard to the molar ratio of 2-methyl-3-butenenitrile to linear pentenenitrile, depending on the composition of the feed stream, can be adjusted in a technically simple manner via the temperature, the
10 pressure and the reflux ratio in the distillation.

The temperature in the region of the isomerization zone which, in the case of a distillation apparatus as a reaction vessel, is the bottom region, may advantageously be at least 10°C, more advantageously at least 60°C, preferably at least 100°C, in
15 particular at least 110°C.

The temperature in the region of the isomerization zone which, in the case of a distillation apparatus as a reaction vessel, is the bottom region, may advantageously be at most 200°C, more advantageously at most 150°C, preferably at most 140°C, in
20 particular at most 130°C.

The pressure in the region of the isomerization zone which, in the case of a distillation apparatus as a reaction vessel, is the bottom region, may advantageously be at least 5 mbar, more advantageously at least 200 mbar, preferably at least 500 mbar, in
25 particular at least 600 mbar.

The pressure in the region of the isomerization zone which, in the case of a distillation apparatus as a reaction vessel, is the bottom region, may advantageously be at most 1000 mbar, more advantageously at most 950 mbar, preferably at most 900 mbar, in
30 particular at most 1000 mbar.

The pressure specified may likewise be attained as the partial pressure of the nitrile stream by passing in an inert gas such as nitrogen or argon (stripping effect).

The stream comprising 2-methyl-3-butenenitrile and linear pentenenitrile withdrawn
35 from the isomerization may advantageously be separated into a first stream comprising 2-methyl-3-butenenitrile, the proportion by weight of 2-methyl-3-butenenitrile in this stream being higher than in said withdrawal stream, and a second stream comprising linear pentenenitrile, the proportion by weight of linear pentenenitrile in this stream being higher than in said withdrawal stream.

This separation can be effected by separating processes known per se, such as distillation, extraction, crystallization, advantageously by distillation.

- 5 Useful apparatus for the distillation is apparatus customary for this purpose, as described, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 7, John Wiley & Sons, New York, 1979, page 870-881, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or columns having random packing.

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The composition of the first stream with regard to the proportion by weight of 2-methyl-3-butenenitrile and of the second stream with regard to the proportion by weight of pentenenitrile, depending on the composition of the feed stream, can be adjusted in a technically simple manner via the temperature, the pressure and the reflux ratio in the

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In a preferred embodiment, the first stream should have a proportion by weight of 2-methyl-3-butenenitrile of at least 50% by weight, preferably at least 70% by weight, in particular at least 90% by weight.

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In a preferred embodiment, the second stream should have a proportion by weight of linear pentenenitrile of at least 50% by weight, preferably at least 70% by weight, in particular at least 90% by weight.

- 25 In a preferred embodiment, the first stream can be fed to an isomerization of the process according to the invention, in particular into the process according to the invention.

30 The achievement of the object underlying the present invention by the process according to the invention was surprising, since the boiling point of 2-methyl-3-butenenitrile at 124°C (atmospheric pressure) is lower than the boiling point of 3-pentenenitrile (144°C, atmospheric pressure) and, inspite of this, the 3-pentenenitrile obtained in the isomerization can be removed from the mixture via the gas phase distillatively.

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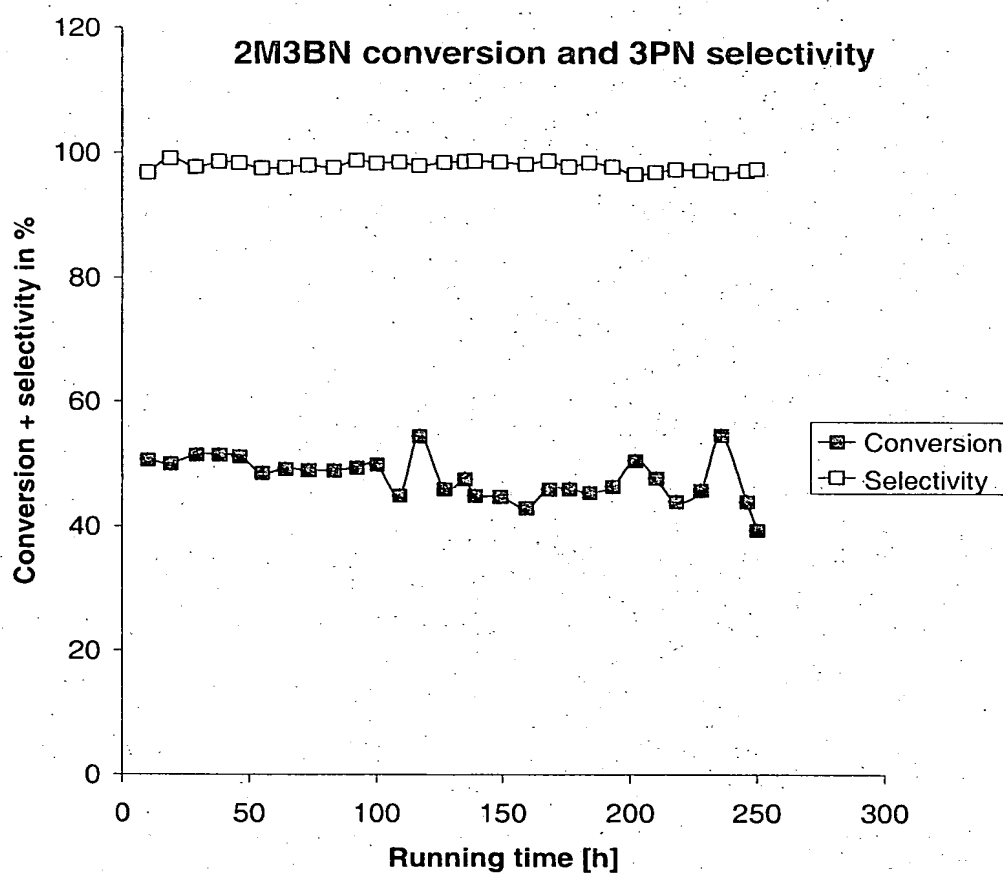
Examples

A stirred tank was initially charged with 97 g of the nickel tetrakis(m/p-tolyl)-(o-isopropylphenyl) phosphite catalyst. 80 g/h of liquid 2-methyl-3-butenenitrile were

added continuously to this catalyst at a reactor temperature of 130°C. A vacuum pump was used to set a pressure of 750-800 mbar. A thermostat at $T = 143^{\circ}\text{C}$ was used to feed sufficient energy to remove 80 g/h. of a nitrile mixture consisting of 2-methyl-3-butenitrile ("2M3BN") and 3-pentenitrile ("3PN") (for composition over time see graph 1) in gaseous form. The reactor contents were a constant 225 ml. The nitrile was subsequently separated at atmospheric pressure into 2-methyl-3-butenitrile (top) and 3-pentenitrile (bottom).

The mixture composition is plotted in graph 1.

Graph 1



We claim:

1. A process for isomerizing 2-methyl-3-butenitrile to linear pentenenitrile in the presence of a system comprising
 - a) Ni(0)
 - b) a trivalent phosphorus-containing compound which complexes Ni(0) as a ligand and
 - c) a Lewis acid,which comprises withdrawing a mixture comprising 2-methyl-3-butenitrile and linear pentenenitrile from the reaction mixture during the isomerization.
2. A process as claimed in claim 1, wherein the isomerization is carried out at a temperature in the range from 10 to 200°C.
3. A process as claimed in claim 1, wherein the isomerization is carried out at a temperature in the range from 100 to 150°C.
4. A process as claimed in any of claims 1 to 3, wherein the isomerization is carried out at a pressure in the range from 5 to 1000 mbar.
5. A process as claimed in any of claims 1 to 4, wherein, during the isomerization, a stream comprising 2-methyl-3-butenitrile is added to the reaction mixture and a stream comprising 2-methyl-3-butenitrile and linear pentenenitrile is withdrawn from the reaction mixture, the withdrawal stream having a lower proportion by weight of 2-methyl-3-butenitrile than the feed stream.
6. A process as claimed in any of claims 1 to 5, wherein the withdrawal stream comprising 2-methyl-3-butenitrile and linear pentenenitrile is subsequently separated into a first stream comprising 2-methyl-3-butenitrile, the proportion by weight of 2-methyl-3-butenitrile in this stream being higher than in said withdrawal stream, and a second stream comprising linear pentenenitrile, the proportion by weight of linear pentenenitrile in this stream being higher than in said withdrawal stream.

7. A process as claimed in claim 6, wherein the first stream is fed to an isomerization as claimed in any of claims 1 to 5.
8. A process as claimed in any of claims 1 to 7, wherein the linear pentenenitrile obtained is cis-2-pentenenitrile, trans-2-pentenenitrile, cis-3-pentenenitrile, trans-3-pentenenitrile, 4-pentenenitrile or a mixture thereof.
9. A process as claimed in any of claims 1 to 7, wherein the linear pentenenitrile obtained is cis-3-pentenenitrile, trans-3-pentenenitrile, 4-pentenenitrile or a mixture thereof.
10. A process as claimed in any of claims 1 to 7, wherein the linear pentenenitrile obtained is cis-3-pentenenitrile, trans-3-pentenenitrile or a mixture thereof.

Abstract

A process for isomerizing 2-methyl-3-butenitrile to linear pentenenitrile in the presence of a system comprising

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- a) Ni(0)
- b) a trivalent phosphorus-containing compound which complexes Ni(0) as a ligand and
- c) a Lewis acid,

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which comprises withdrawing a mixture comprising 2-methyl-3-butenitrile and linear pentenenitrile from the reaction mixture during the isomerization.